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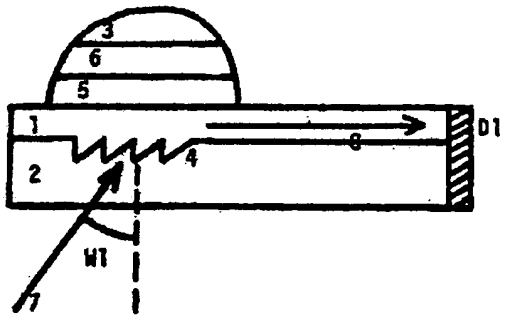
(54) Sensor for Selective Detection of Substances in Gaseous, Liquid or Solid Measurement Substances

(57) The inventive sensor for selective detection of substances in gaseous, liquid or solid measurement substances is composed of integrated optical elements. As the waveguide structure, it consists of a waveguide film (1), a substrate (2), a diffraction grating (4) and a selectively sensitive substance (5) which is applied to the waveguide film (1) at least in the area of the diffraction grating (4) and/or is introduced into pores of a porous waveguide film (1) at least in the area of the diffraction grating (4). The measurement substance (3) can be brought into contact with the selectively sensitive substance (5) at least in the area of the grating. The sensor principle consists of depositing the substance that is to be detected and is present in the measurement substance (3) onto the selectively sensitive substance to induce a change in the effective refractive index N of a mode (8) propagating in the waveguide film (1). To detect this change, the arrangement (1, 2, 3, 4, 5) consisting of the waveguide structure and the measurement substance is used as a grating input coupler and/or a grating output coupler or a Bragg reflector.



PATENT CLAIMS

1. A sensor for selective detection of substances in gaseous, liquid or solid measurement substances, characterized in that it consists of a waveguide film (1), a substrate (2), at least one diffraction grating which functions as a grating coupler or as a Bragg reflector and a selectively sensitive substance (5) which is applied to the waveguide film (1) at least in the area of the diffraction grating (4) and/or is introduced into pores of a porous waveguide film (1) at least in the area of the diffraction grating (4); it is also constructed as a waveguide structure in the area of the diffraction grating (4), and the measurement substance (3) can be brought into contact with the selectively sensitive substance (5) at least in the area of the diffraction grating (4), whereby the selectively sensitive substance (5) is selected so that it binds the substance that is to be detected and is present in the measurement substance (3) to itself by chemical bonding or by chemisorption, adsorption or absorption.

2. The sensor according to Claim 1, characterized in that the selectively sensitive substance (5) is selected so that it reversibly binds to the substance that is to be detected and is present in the measurement substance (3) so that the substance to be detected is desorbable.

3. The sensor according to Claim 1 or 2, characterized in that diffraction grating (4) is a phase volume grating.

4. The sensor according to Claim 1 or 2, characterized in that the diffraction grating (4) is a surface relief grating.

5. The sensor according to Claim 1 or 2, characterized in that the refractive index of the waveguide film (1) is selected to achieve a high sensitivity at least 1%, but preferably more than 10%, greater than that of the substrate (2) .

6. The sensor according to one of Claims 1, 2 or 5, characterized in that the waveguide film (1) is covered with a protective film (12) outside of the area of the diffraction grating to partially or completely prevent an influence on a mode (8) which is propagating outside of the area of the diffraction grating (4).

7. The sensor according to Claim 6, characterized in that the protective layer (12) increases in the form of a taper outside of the grating region.

8. The sensor according to one of Claims 1, 5 or 6, characterized in that the selectively sensitive substance (5) consists of molecules of a certain antigen which selectively bind the antibodies corresponding to this antigen from the measurement substance, or the selectively sensitive substance (5) consists of molecules of a certain antibody which selectively bind the antigen corresponding to this antibody.

9. Use of the sensor according to one of Claims 1 through 8 for selective detection of substances in gaseous, liquid or solid measurement substances, characterized in that the changes

in the effective refractive index of a mode (8, 10, 11) propagating in an arrangement consisting of a waveguide structure and a measurement substance (3) are measured, said changes being brought about by effective chemical bonds or chemisorption, adsorption or absorption processes taking place in and/or on the selectively sensitive substance (5).

10. Use according to Claim 9, characterized in that a laser beam (5) which is directed at the diffraction grating (4) at a fixed selected angle of incidence (W1) is input into the waveguide film (1) through this diffraction grating (4) and the changes in the effective refractive index of the mode (8) brought about due to the processes taking place in and/or on the selectively sensitive substance (5) are determined by measuring the changes in intensity of the mode (8).

11. Use according to Claim 9, characterized in that an angle of incidence (W1) at which the laser beam (7) is directed at the diffraction grating (4) is readjusted while the processes are taking place in and/or on the selectively sensitive substance so that the mode (8) has the greatest possible intensity, and the changes in the effective refractive index of the mode (8) are determined from the change in the angle of incidence (W1).

12. Use according to Claim 9, characterized in that the mode (8) is output from the waveguide film (1) through the diffraction grating (4), and the change in the effective refractive index brought about due to the processes taking place in and/or on the selectively sensitive substance (3) are determined by measuring the changes in the output angle (W2), or at a fixed output angle (W2) the changes in the intensity of an output laser beam (9) are recorded.

13. Use according to Claim 9, characterized in that the mode (8) is directed at the diffraction grating (4) and a Bragg angle (W3) and is Bragg-reflected on the diffraction grating (4), and the changes in the effective refractive index brought about due to the processes taking place in and/or or the selectively sensitive substance (5) are determined by measuring the changes in intensity of the reflected mode (10) and/or the transmitted mode (11).

14. Use according to one of Claims 10, 11 or 13, characterized in that the intensity of the mode (6 [sic; 8]) is determined by having the mode (8) be output through a second diffraction grating (15) and measuring the intensity of the output laser beam (17) using a detector (D6).

15. Use according to one of Claims 10, 11 or 13, characterized in that the intensity of the mode (8, 10, 11) is determined by passing the mode (8, 10, 11) through an end face so that it directly strikes a detector (D1, D3, D4) on this end face, with the intensity of the incident mode (8, 10, 11) being measured by the detector (D1, D3, D4).

DESCRIPTION

The present invention relates to a sensor according to the preamble of Patent Claim 1. An ellipsometer is a known device for detecting chemisorbate layers or chemically bound layers on surfaces; it analyzes the polarization of light reflected on the chemisorbate layer. This device takes up relatively little space and the required measurement volume is relatively large, which can be a great disadvantage in the case of expensive measurement substances. In addition, the measurement accuracy is limited because the measurement cell influences the polarization of the light.

Another method of detecting chemical substances is spectrophotometry. E. E. Hardy et al. describe a spectrophotometer (*Nature* 257 (1975), 666-667) in which light is guided in an optical waveguide. The optical waveguide in this case is a quartz rod having macroscopic dimensions (the diameter of the quartz rod is approx. 1 mm), i.e., it is a typical multimode waveguide. The measurement method is based on the change in light transmission of the optical waveguide due to adsorption of a chemical substance on the quartz rod, which has a chemically sensitive layer.

This invention, as characterized in Patent Claim 1, solves the problem of creating a sensor which

1. will permit selective detection of substances in gaseous, liquid or solid measurement substances;

2. is capable of resolving changes in surface coverage down to approximately one hundredth of a monomolecular layer;

3. requires a very small measurement volume;

4. takes up the smallest possible amount of space.

This invention is explained in greater detail below on the basis of drawings, which show:

Figure 1: a schematic diagram of the basic elements of this invention;

Figure 2: an inventive measurement device having a grating input coupler;

Figure 3: an inventive measurement device having a grating output coupler;

Figure 4: an inventive measurement device having a Bragg reflector;

Figure 5: a schematic diagram of the basic elements of this invention, whereby the waveguide is covered with a protective layer outside of the grating region;

Figure 6: an inventive device for measuring the intensity of the guided light wave, whereby scattered light generated by the guided light wave is collected by fiber optics and sent to a detector;

Figure 7: an inventive device for measuring the intensity of the guided light wave, whereby the guided light wave is output through a second diffraction grating.

The basic component of the integrated optics is the planar waveguide, which consists of a thin dielectric layer on a substrate. Input laser light can be guided in this thin layer by total reflection. The rate of propagation of such a guided light wave (referred to below as a "mode") amounts to c/N, where c is the velocity of light and N is the effective refractive index of the mode propagating in the waveguide. The effective refractive index N is determined by the configuration of the waveguide (layer thickness and refractive index of the thin layer and the refractive index of the substrate).

The sensor principle is based on the fact that a change in configuration of the waveguide produces a change in the effective refractive index N, which is to be interpreted as a complex variable. A change in configuration may occur due to deposition of an additional layer onto the thin layer because a deposited additional layer has the effect of an increase in layer thickness of the thin layer.

Selective detection of substances can be accomplished by applying a selectively sensitive substance in the form of an additional layer to the thin layer, where this additional layer selectively binds a substance that is present in the measurement substance and is to be detected and it does so by chemical bonding or by chemisorption, adsorption or absorption, therefore resulting in an increase in thickness of this additional layer and thus also a change in the effective refractive index. A change in effective refractive index induced in this way can be detected with a grating input coupler and/or a grating output coupler, for example, or with a Bragg reflector. The mechanism of action of the grating coupler and/or the Bragg reflector is described below on the basis of the figures.

Figure 1 shows a schematic diagram of the basic elements of this invention. A thin layer is provided in the form of a planar waveguide film 1 (e.g., a vitreous SiO_2-TiO_2 layer) on a substrate 2 (e.g., a borosilicate glass). The waveguide film 1 and the substrate 2 together form the so-called waveguide 1/2. In order for laser light to propagate via total reflection in the waveguide film 1, the refractive index of the waveguide film 1 must be greater than that of the adjacent media (i.e., substrate 2, measurement substance 3). The waveguide film 1 may have a microporous structure such as that which can be achieved in film production with a dip coating method, for example. A diffraction grating 4 of the length L is provided on the surface of the waveguide film 1 which faces either the substrate 2 or the measurement substance 3 or it may be provided in the volume of the waveguide film (for details regarding production of the waveguide and the diffraction grating, see, for example, W. Lukosz and K. Tiefenthaler, *Optics Letter* 8 (1983), 537-539).

The diffraction grating 4 is used for diffraction of laser light, wherein this diffraction is influenced to a significant extent by the effective refractive index N.

The waveguide film 1 is covered with a selectively sensitive substance 5 in the form of an additional layer, at least in the area of the grating; this permits selective detection of a substance present in the measurement substance 3. The substance 3 to be investigated, which is also referred to as the "measurement substance," is applied to the selectively sensitive substance 5, at least in the area of the diffraction grating 4.

The properties of the selectively sensitive substance 5 are such that it selectively chemically binds or chemisorbs, adsorbs or absorbs only one certain substance which is present in the measurement substance 3. The substance bound in this way forms another additional layer 6. This selectivity can be used, for example, to identify antigen-antibody coupling in biochemistry. If the selectively sensitive substance 5, which is in the form of an additional layer in the present example, consists of a certain antigen, then an antigen-antibody coupling takes place when the antibody corresponding to the antigen is present in the measurement substance 3. The other additional layer 6 in this example consists of antibodies. The function of the antigen and antibodies may also be interchanged, i.e., the selectively sensitive substance 5 may be composed of antibodies.

The chemically binding or chemisorbent, adsorbent or absorbent selectively sensitive substance 5 may be in the form of an additional layer and/or may be present only in the micropores of the waveguide film 1. In the latter case, the chemical binding or the chemisorption, adsorption or absorption takes place in the waveguide film 1 itself. If the micropores are filled with a picrate dye, for example, then cyanic vapors can be detected selectively with the present sensor (see E. E. Hardy et al., *Nature* 257 (1975), 666-667). In this example, selective adsorption is also associated with a change in color of the selectively sensitive substance.

According to Figure 2, a laser beam 7 may be input into a waveguide 1/2 through a diffraction grating 4 and travel along the waveguide 1/2 in the form of a mode 8. It does not matter whether the laser beam 7 strikes the diffraction grating 4 from the substrate side or from the measurement substance side. Suitable lasers for use here include, for example, a helium neon laser or a semiconductor laser. The input condition is a resonance condition and is characterized in that the angle of incidence W1 of the laser beam 7 must be selected accordingly, depending on the waveguide configuration, i.e., the effective refractive index, to achieve a maximum intensity of the mode 8. The angle of incidence W1 of the laser beam 7 is consequently determined by the effective refractory index N of the excited mode 8, which is determined essentially by the refractive indices of the media involved in the waveguide, the layer thickness of the waveguide film 1 and the refractive index and layer thickness of the selectively sensitive substance 5 in the

form of the additional layer and the other additional layer 6. For example, if the effective refractive index N of the mode 8 is altered due to a chemisorption or desorption process, then the angle of incidence W1 selected originally is no longer optimum, so that the intensity of the mode 8 changes. The change in the effective refractive index N can then be measured by two different methods.

At small effective refractive index changes, the change in the light intensity of the mode 8 can be measured with the help of a detector D1, so it is possible to deduce the change in the effective refractive index and thus the status of the chemisorption or desorption process. This measurement method is suitable for measuring effective refractive index changes, which are smaller than the half-width of the resonance input curve. The half-width of the resonance input curve depends on the length L of the diffraction grating because of the uncertainty principle (see K. Tiefenthaler and W. Lukosz, *Optics Letters* 9 (1984), 137-139). At a grating length of L = 6 mm and a wavelength of 633 nm, changes in the surface coverage amounting to one-hundredth of a monomolecular layer, e.g., of a layer of H_2O, can still be resolved.

In the case of changes in the effective refractive index amounting to more than the half-width of the resonance input curve, registration takes place by optimizing the light intensity of mode 8 by readjusting the angle of incidence W1 of laser beam 7 so that the intensity of mode 8 is always at a maximum. Because of the change in the angle of incidence W1, it is possible to deduce the change in the effective refractive index of mode 8. There is also the possibility of selecting the angle of incidence W1 on the basis of calculations, so that a mode 8 of maximum intensity is obtained only when the thickness of the other additional layer has reached a desired value.

Figure 3 shows an inventive measurement device having a grating output coupler. Waveguide 1/2, diffraction grating 4 and selectively sensitive substance 5 in the form of the additional layer are described in conjunction with Figure 1. If a mode 8 strikes the diffraction grating 4, the mode 8 is partially or completely output. The output laser beam 9 emerges from the waveguide 1/2 at a certain output angle W2, which is determined by the effective refractive index of mode 8. The generation of mode 8 is not depicted in Figure 3. The mode can be excited, for example, by end-face input coupling, prism input coupling, grating input coupling, etc. (see T. Tamir, *Integrated Optics*, chapter 3). A change in the layer thickness of the other additional layer 6 produces a change in the effective refractive index of mode 8 in the grating region, which results in a change in the output angle W2. This change in the output angle W2 can be measured with a diode array D2, for example, or with another position-sensitive detector.

Figure 4 shows a so-called Bragg reflector. The diffraction gratings used for the grating coupler (Figure 2 and 3) may also be used as Bragg reflectors. For reasons of space, Figure 4 does not show the selectively sensitive substance 5 or the other additional layer 6. A mode 8 is

reflected on a diffraction grating if the Bragg condition is met, i.e., if the angle of incidence W3 corresponds to the Bragg angle (see W. Lukosz and K. Tiefenthaler, *Optics Letter* 8 (1983), 537-539). For the generation of mode 8, the same thing applies as that said regarding Figure 3. The detectors D3 and D4 measure the intensity of a mode 10 reflected on the diffraction grating 4 and/or the intensity of a transmitted mode 11. The Bragg angle is defined by the effective reactive index N in the grating region. If the effective refractive index N changes because of a chemisorption or desorption process, then the Bragg condition is disturbed. The intensity of the reflected mode and the intensity of the transmitted mode also change. The change in the layer thickness of the other additional layer 6 can be deduced by measuring the light intensity of the reflected mode 10 and/or of the transmitted mode 11 using detectors D3 and/or D4.

Another measurement possibility is to select the angle of incidence W3 so that the Bragg condition is just barely not met and thus there is no reflected mode 10. If the layer thickness of the other additional layer 6 has reached the desired value, a reflected mode 10 occurs because the Bragg condition is then met. The change in the layer thickness of the other additional layer 6 can be deduced on the basis of the angle W3 and the intensity of the reflected mode 10 and/or of the transmitted mode 11.

Adsorbed macromolecules such as proteins may have a high scattering effect on a mode. Therefore, the mode may be diminished to such a great extent outside of the grating region that it is no longer possible to measure the light intensity at all. The same argument also applies, for example, to measurement substances which absorb light weakly. To partially or completely prevent this effect, it is advantageous – as depicted in Figure 5 – to cover the waveguide film 1 with the protective layer 12 outside of the grating region. This protective layer 12 may be a layer of SiO_2, for example. The layer thickness of the protective layer 12 must be so great that the mode can only be reduced or cannot interact at all with measurement substance 3 outside of the grating region. The protective layer 12 may also be used to prevent the interfering influence of the fastening device for a cell (not shown in Figure 5) filled with the measurement substance 3.

Figure 5 also shows that it is advantageous outside of the grating region to have the protective layer 12 increase in the form of a taper (i.e., not in the form of abrupt step).

Figures 2 and 4 show detectors which measure the intensity of modes 8 and/or 10 and 11 directly. To have as much light as possible striking the detectors D1 and/or D3 and D4, the detectors should be situated as close as possible to the point of outlet where the mode leaves the waveguide 1/2 as depicted in Figures 2 and 4. It is also advantageous if the waveguide film 1 ends at the same point as the substrate, i.e., if the substrate 2 does not extend beyond the waveguide film 1.

Another detection option is illustrated in Figure 6, where the scattered light 13 generated by mode 8 is collected by fiber optics 14 and sent to a detector D5. The intensity of the scattered

light 13 is proportional to the intensity of the mode 8. The scattered light 13 is always present because of unavoidable inhomogeneities in the waveguide film 1. Instead of direct measurement of the intensity of mode 10 and/or mode 11, the intensity of the scattered light of the reflected mode 10 and/or of the transmitted mode 11 can be measured in the same way with a Bragg reflector (see Figure 4).

There is also the possibility – as depicted in Figure 7 – for the mode 8 to be output with a second diffraction grating 15, for example, and then for the intensity of the laser beam 17, which is output at an angle W4, to be measured by using a detector D6. This intensity is proportional to the intensity of the mode 8. The output coupling mechanism of the second diffraction grating 15 must not be disturbed by the measurement substance 3. This can accomplished, for example, by having a protective layer 14 separating the waveguide 1/2 from the measurement substance 3 in the region of the second diffraction grating 15 or by no measurement substance 3 being present at all in this grating region (for details regarding the protective layer, see comments regarding Figure 5). Output, however, may also be accomplished via a prism coupler or a taper (see T. Tamir, *Integrated Optics*, chapter 3).

The sensitivity of the integrated optical sensor can be defined as a differential change in the effective refractive index on the basis of a differential change in layer thickness in the other additional layer 6. Especially high sensitivities are achieved when the waveguide film 1 has a much higher refractive index than the substrate 2 and the measurement substance 3 and when the layer thickness of the waveguide film 1 is somewhat greater than the minimum thickness. A minimum layer thickness (the so-called cut-off layer thickness) is necessary for the waveguide film 1, in order to be able to excite a mode in a waveguide film 1 at all (see T. Tamir, *Integrated Optics*, Springer, Berlin, 1979, chapter 2). To achieve highest possible sensitivity, it is advisable to select the refractive index of the waveguide film 1 to be at least 1%, but preferably more than 10%, greater than that of the substrate 2.

Fig. 1

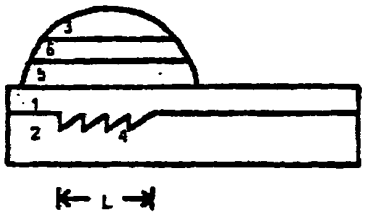


Fig. 2

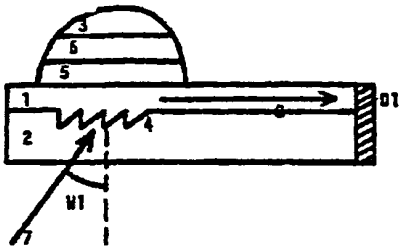


Fig. 3

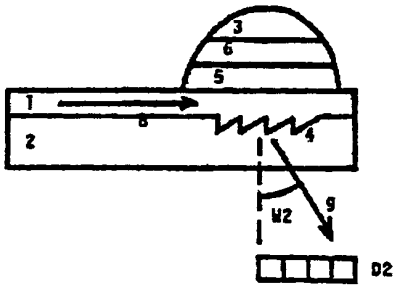


Fig. 4

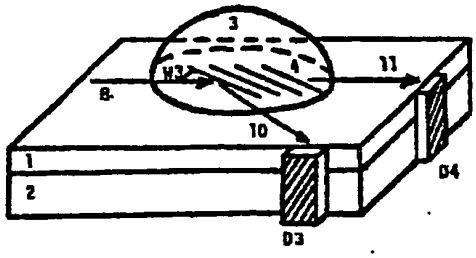


Fig. 5

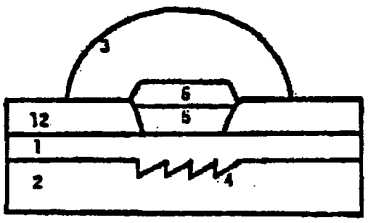


Fig. 6

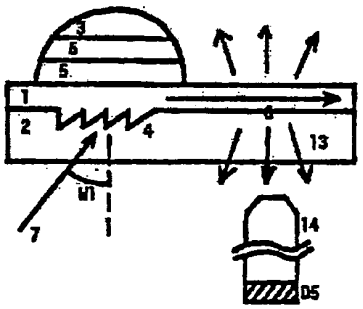


Fig. 7